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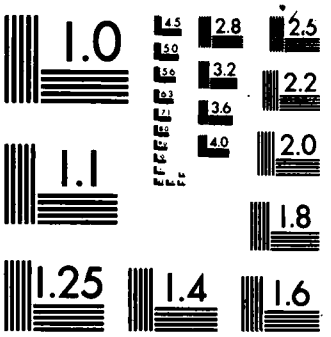

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Substitution and Addition Reactions of a (Methylene)phosphine with Alkyllithium Reagents

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Bi-L. Li and R.H. Neilson

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Treatment of the (methylene)phosphine $(Me_3Si)_2NP{=}CHSiMe_3$ (1) with alkyllithium reagents and Me_3SiCl affords either the diphosphinomethane derivative $R_2P\text{-}CH(SiMe_3)\text{-}P(R)CH(SiMe_3)_2$ (2, R = Me) or the trialkylphosphine $R_2PCH(SiMe_3)_2$ (3, R = t-Bu). A reaction pathway involving both nucleophilic substitution and addition reactions at the P=C moiety is suggested. Compound 2 exhibits hindered rotation about the $P\text{-}CH(SiMe_3)_2$ bond with a measured $\Delta G_c^{\ddagger}$ of 17.7 kcal/mole.

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Abstract

Treatment of the (methylene)phosphine $(Me_3Si)_2NP=CHSiMe_3$ (1) with alkyllithium reagents and Me_3SiCl affords either the diphosphinomethane derivative $R_2P-CH(SiMe_3)-P(R)CH(SiMe_3)_2$ (2, R = Me) or the trialkylphosphine $R_2PCH(SiMe_3)_2$ (3, R = t-Bu). A reaction pathway involving both nucleophilic substitution and addition reactions at the P=C moiety is suggested. Compound 2 exhibits hindered rotation about the $P-CH(SiMe_3)_2$ bond with a measured $\Delta G_c^{\ddagger}$ of 17.7 kcal/mole.

delta G+ sub c

Many recent reports have dealt with the preparative chemistry of (methylene)phosphines $RP{=}CR'_2$ as well as their structural and bonding characteristics.[1] Moreover, some relatively clear and consistent patterns of reactivity of such compounds are now emerging. The types of reactions of (methylene)phosphines reported thus far include: (1) addition of polar electrophilic reagents to the P=C bond[2], (2) oxidation to 3-coordinate P(V) derivatives[3], (3) complexation of transition metals to the phosphorus lone pair or to the P=C π bond[4], and (4) various cycloaddition processes such as Diels-Alder reactions.[5] In another general mode of reactivity, we find that these coordinatively unsaturated phosphorus compounds will also react smoothly with nucleophiles.[6] We report here some novel examples involving both substitution and addition reactions of a bis(trimethylsilyl)amino substituted (methylene)phosphine with alkyllithium reagents.

Treatment of [bis(trimethylsilyl)amino](trimethylsilyl-methylene)phosphine[2c] $\underset{\sim}{1}$ in Et_2O at -78°C with MeLi, followed by quenching with Me_3SiCl, does not yield the expected[7] phosphine $(Me_3Si)_2NP(Me)CH(SiMe_3)_2$. Instead, the reaction takes a much more complicated course, forming the novel diphosphinomethane derivative $\underset{\sim}{2}$ (eq 1). The product $\underset{\sim}{2}$ is isolated as a colorless liquid in 88% yield by fractional distillation. The characterization of $\underset{\sim}{2}$ is based mainly on NMR data (Table I) with the AB pattern in the ^{31}P NMR spectrum being especially diagnostic. A satisfactory elemental analysis and the

appropriate mass spectral fragmentation pattern were also obtained for 2.

$$2\ (Me_3Si)_2NP{=}CHSiMe_3 \quad (\underset{\sim}{1}) \quad + \quad 3\ MeLi \quad + \quad 3\ Me_3SiCl \longrightarrow$$

$$Me_2P{-}CHSiMe_3 \quad (\underset{\sim}{2}) \quad + \quad 3\ LiCl \quad + \quad 2\ (Me_3Si)_3N \qquad (1)$$

Under similar conditions, the reaction of 1 with t-BuLi occurs in a 1:2 stoichiometry (eq 2) to afford the di(t-butyl)-phosphine 3 in 69% yield rather than a P-C-P product analogous to 2.

$$(Me_3Si)_2NP{=}CHSiMe_3 \quad (\underset{\sim}{1}) \quad + \quad 2\ t\text{-}BuLi \quad + \quad 2\ Me_3SiCl \longrightarrow$$

$$(t\text{-}Bu)_2P{-}CH(SiMe_3)_2 \quad (\underset{\sim}{3}) \quad + \quad 2\ LiCl \quad + \quad (Me_3Si)_3N \qquad (2)$$

These remarkably clean reactions of the (methylene)phosphine 1 with alkyllithium reagents must involve both nucleophilic displacement of the bis(trimethylsilyl)amide group as well as addition across the P=C bond. The reaction pathway proposed in Scheme I is strongly suggested by the following experimental observations: (1) The byproduct $(Me_3Si)_3N$ can be isolated and identified by NMR, indicating that $(Me_3Si)_2NLi$ is indeed formed.[8]

Moreover, the ^1H NMR integration of the crude reaction product is consistent with the stoichiometry given by equation 1. (2) The use of 1:1 mole ratios of 1 to RLi yields only unreacted 1 in addition to products 2 or 3. (3) The formation of 3 in the t-BuLi reaction rather than a product similar to 2 is consistent with increased steric hindrance at phosphorus in intermediates A and B when R = t-Bu. (4) When the reaction with MeLi is monitored by low-temperature ^{31}P NMR, the (methylene)phosphine intermediate A is not seen but an AB pattern (δ_A -1.8, δ_B -6.8, J_{AB} = 69.3 Hz) assignable to the diphosphorus anion C is clearly observed prior to the addition of Me_3SiCl.

A final point of interest concerns the ^1H and ^{13}C NMR spectra of the di(t-butyl)phosphine 3 which reveal non-equivalence of the t-Bu signals at room temperature. A high temperature ^1H NMR study shows that the two t-butyl doublets coalesce to a single doublet at 65°C (in C_6H_6 solution) indicating a barrier to rotation about the P-CH$(SiMe_3)_2$ bond of approximately 17.7 kcal/mole. The extreme steric hindrance caused by the bis(trimethylsilyl)methyl group in phosphorus (III) compounds has been previously noted.[9]

Experimental Section

Materials and General Procedures. The (methylene)phosphine 1 was prepared according to the published procedure.[2c] Alkyllithium reagents were used as received from commercial sources. Ether and hexane were distilled from CaH_2 prior to use.

Proton NMR spectra were recorded on a Varian EM-390 spectrometer; ^{13}C and ^{31}P, both with ^{1}H decoupling, were obtained on a JEOL FX-60 instrument. Mass spectral data were obtained on Finnigan OWA 1020 GC-MS system. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

All reactions and other manipulations were carried out under an atmosphere of dry nitrogen or under vacuum. The procedures described below are typical of those which gave the best yields of compounds 2 and 3. Preliminary experiments using equimolar quantities of 1 and the alkyllithium reagents afforded the same products together with unreacted (methylene)phosphine.

Reaction of 1 with MeLi. Methyllithium (30 mmol, 21.5 mL, 1.4 M in Et_2O) was added at -78°C to a stirred solution of 1 (20 mmol, 5.6 g) in Et_2O (50 mL) to yield a light yellow precipitate, presumably anion C (Scheme I). After stirring the mixture for 2.5 h at -78°C, Me_3SiCl (30 mmol, 3.8 mL) was added and the mixture was allowed to warm to room temperature. After stirring overnight, Et_2O was removed under vacuum and hexane (20 mL) was added. The mixture was then filtered and the solvent and $(Me_3Si)_3N$ (identified by ^{1}H NMR) were removed under vacuum. Distillation through a short path column afforded compound 2 as a colorless liquid (3.1 g, 87% yield, bp 99-105°C/0.05 mm). Anal. Calcd: C, 47.73; H, 10.80. Found: C, 47.51; H, 10.77. Mass spectrum, m/e (relative intensity): 352 (2), 337 (9), 291 (22), 279 (6), 205 (4), 193 (10), 147 (14), 73 (100).

Reaction of 1 with t-BuLi. By means of a similar procedure, 1 (20 mmol) was treated with t-BuLi (40 mmol, 22.2 mL, 1.8 M in pentane) at -78°C in Et_2O (50 mL). After quenching with Me_3SiCl (40 mmol) and work-up as described above, distillation gave 3 as a colorless liquid (4.2 g, 69% yield, bp 82-83°C/0.15 mm). Anal. Calcd: C, 59.21; H, 12.17. Found: C, 59.08; H, 12.05. Mass spectrum, m/e (relative intensity): 304 (22), 289 (25), 248 (81), 159 (28), 145 (14), 73 (100).

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Table I. NMR Spectroscopic Data[a]

		^1H		^{13}C		^{31}P
compd	Signal	δ	J_{PH}	δ	J_{PC}	δ
$Me_2P-CHSiMe_3$	$\underline{Me}_3SiC$	0.14	1.0	2.56	5.4,	-23.7[b],
$P-CH(SiMe_3)_2$					1.8	-37.9
Me						
2	$(\underline{Me}_3Si)_2C$[c]	0.10	0.4	1.89	6.7	
				3.49	2.4	
	$\underline{Me}_2P$[c]	1.15	4.8	d		
		1.16	4.2			
	$\underline{Me}P$	1.30	6.0	d		
	$Si_2\underline{C}H$	1.04	2.4	d		
	$P_2\underline{C}H$	e		22.80	48.0,	
					33.3	
$(\underline{t}\text{-}Bu)_2P-CH(SiMe_3)_2$	Me_3Si[c]	0.12	0.2	2.48	11.0	47.6
3		0.18		5.12		
	CH	1.15	13.5	28.67	55.6	
	$\underline{Me}_3C$[c]	1.17	12.3	30.20	14.0	
		1.09	10.8	32.02	16.5	
	$Me_3\underline{C}$[c]			30.95	30.5	
				32.42	17.1	

[a] Chemical shifts are downfield from Me_4Si for ^1H and ^{13}C spectra and from H_3PO_4 for ^{31}P spectra; coupling constants in Hz. Solvents: ^1H, CH_2Cl_2; ^{13}C and ^{31}P, $CDCl_3$.

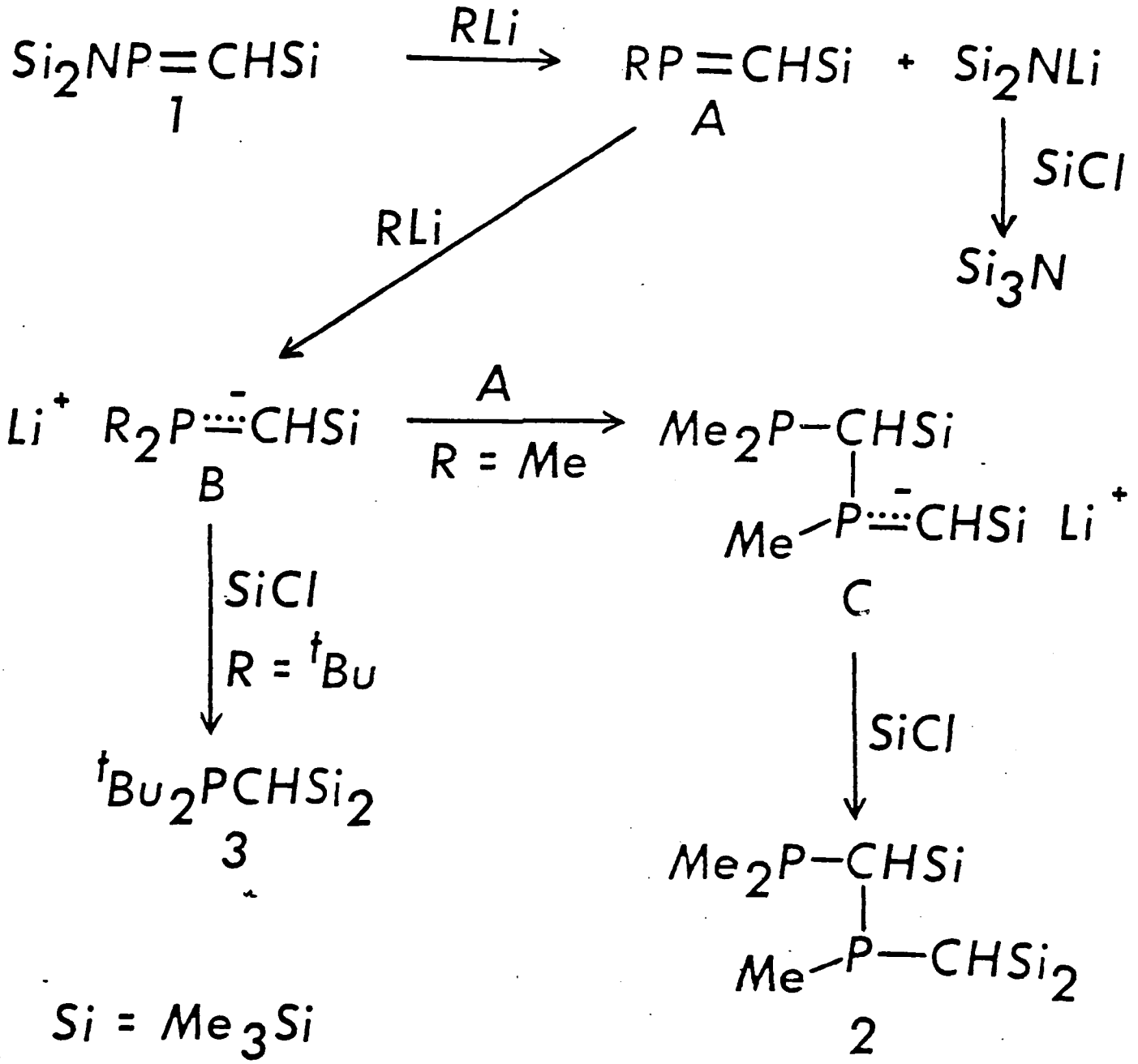
[b] AB pattern with J_{PP} = 95.2 Hz.

[c] Diastereotopic groups observed in ^1H and/or ^{13}C NMR spectra.

[d] Multiplet of ca. 16 overlapping peaks in range δ 9.8 - δ 15.1.

[e] Signals obscured by MeP resonances.

Scheme I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RLi
RP=CHSi
A
+ Si2NLi
SiCl
Si3N
RLi
Li+ R2P⁻=CHSi
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A
R = Me
Me2P-CHSi
Me-P⁻=CHSi Li+
C
SiCl
R = tBu
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SiCl
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Me-P-CHSi2
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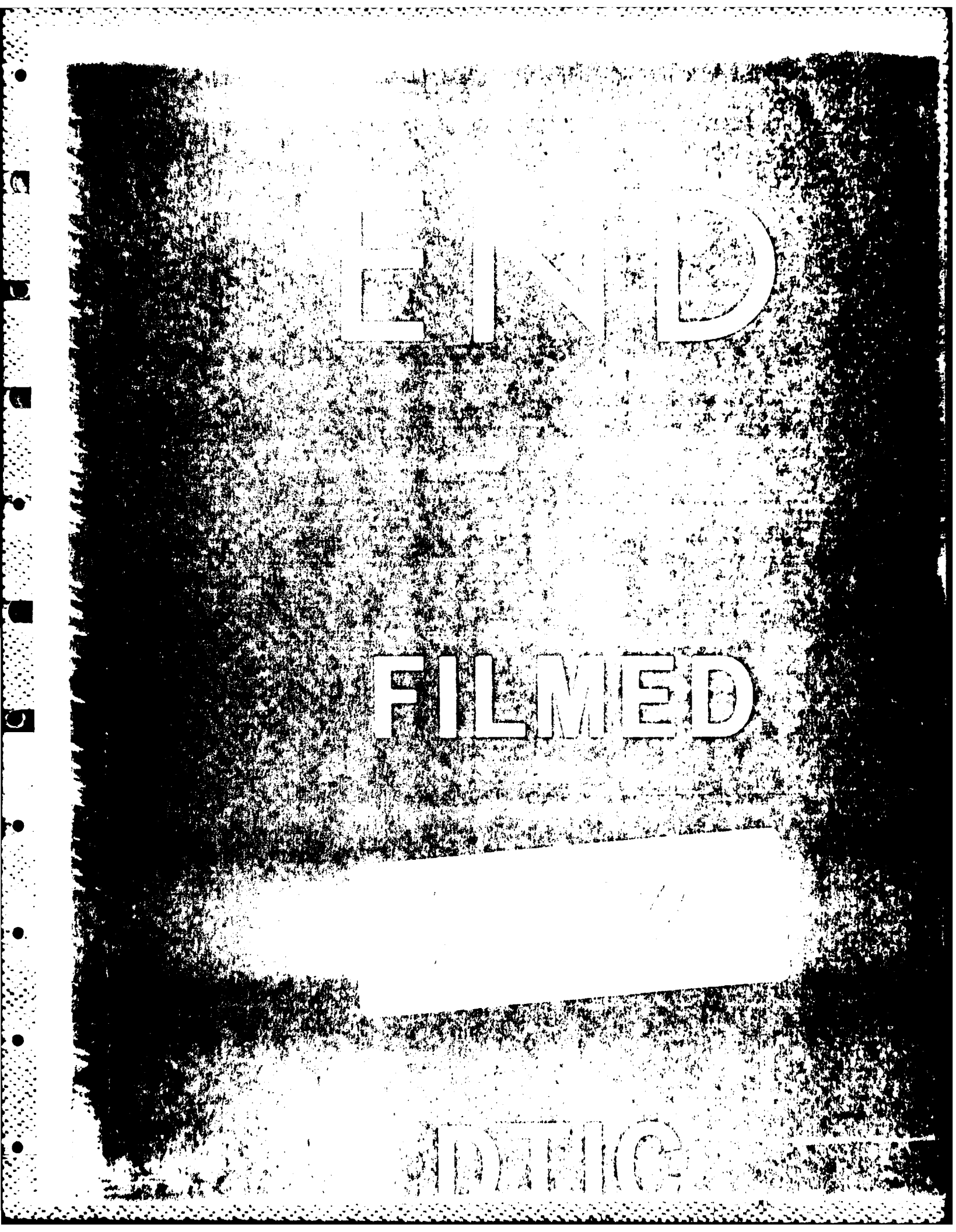
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